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(54) **Crystalline olefin polymers and copolymers in the form of spherical particles at high porosity**

Sphärische, kristalline Olefinpolymere und Copolymere mit hoher Porösität

Polymères et copolymères d'oléfines cristallines sous forme sphéroidale et de haute porosité

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(56) References cited:
EP-A- 0 229 413
EP-A- 0 290 149
EP-A- 0 459 208

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Description

This invention relates to crystalline olefin polymers and copolymers in the form of spherical particles with an average diameter between 50 and 7000 μm and porosity and surface area characteristics which make them suitable for, e.g., the preparation of masterbatches containing significant quantities of pigment and/or additives.

It is known that catalyst components for the polymerization of olefins comprising a titanium compound supported on a magnesium halide in active form can be obtained in spherical particle form suitable for the development of polymers with optimum morphological characteristics. Components of this type are described in U.S. Patents 3,953,414 and 4,399,054.

EP-A-0 459 208, which was published after the priority date of the present application, discloses crystalline copolymers which are propylene copolymers or terpolymers containing more than 85% by weight of propylene. EP-A-0 290 149 discloses propylene/ethylene copolymers containing 2% - 30% ethylene. The polymers are in the form of particles with an average diameter of at least 1 mm and a porosity of at least 0.2 cm^3/g. EP-A-0 229 413 discloses polymers of alpha-olefins in the form of spherical particles having high bulk density and high crystallinity. Also, the polymers obtained with the catalysts of U.S. Patent 4,399,054 are in spherical particle form having high flowability and high bulk density.

The porosity (around 10% expressed in percentage of voids) and the surface area, however, are not sufficiently high to allow their use, particularly in the field of masterbatch preparation when said masterbatch contain a significant quantity of pigments and/or additives.

Now it has been found that it is possible to obtain crystalline olefin copolymers in spherical particle form having various advantages by co-polymerization of olefins of the formula $CH_2 = CHR$ wherein R is hydrogen, an alkyl radical with 2-6 carbon atoms or is aryl such as phenyl or substituted phenyl with another different olefin of the foregoing formula, or may be copolymerized with propylene, wherein the amount of propylene in the resulting copolymer is less than 30% by weight or provided that when ethylene is one of the olefins, it is present in the resulting copolymer in an amount greater than 80% by weight. The crystalline olefin copolymer is in spherical particle form with an average diameter between 50 and 5000 μm, a porosity expressed in percentage of voids which is greater than 15% and preferably is between 15% and 40%, and wherein more than 40% of the pores have a diameter greater than one μm.

The spherical form particles exhibit a lowered degree of crystallinity relative to a polymer of equivalent crystallizability which has undergone melt pelletization. Reduced crystallinity coupled with the highly porous nature of the sphere provides particular benefits when the material is used as a substrate for subsequent reactions.

Typical spherical polymeric materials show the following properties:

- percent porosity = 15-35%;
- particle size distribution = 100% of the spherical particles have a diameter between 1000 and 3000 μm; preferably 40-50% of the particles have a diameter between 1000 and 2000 μm, and 35-45% between 2000 and 3000 μm;
- more than 90% of the pores have a diameter greater than one μm.

The percent porosity is determined by absorption of mercury according to the method described hereinafter.

The catalysts used in the preparation of the foregoing spherical copolymers are obtained from catalyst components having particular morphological properties, including a titanium halide or titanium halo-alcoholate, supported on magnesium chloride.

The spherical catalyst components are obtained from adducts of magnesium chloride with alcohols generally containing 3 moles of alcohol per mole of $MgCl_2$, prepared by emulsifying, in the molten state, the adduct in an inert hydrocarbon liquid immiscible with the melted adduct, then cooling the emulsion in a very short time in order to effect solidification of the adduct in the form of spherical particles.

The particles are then subjected to partial dealcoholization using a heating cycle at a temperature increasing from 50° to 130°C until the alcohol content is reduced from 3 to a value as low as 0.1, preferably from 0.1 to 1.5 moles per mole of $MgCl_2$.

The adducts thus obtained are suspended cold in $TiCl_4$, at a concentration of 40-50 g/l, and then brought to a temperature of 80°-135°C where they are maintained for 1-2 hours.

An electron-donor compound can also be added to the $TiCl_4$ selected, preferably, from the alkyl, cycloaklyl or aryl esters of phthalic acid, such as diisobutyl, di-n-butyl and di-n-octyl phthalate.

The excess $TiCl_4$ is then removed hot through filtration or sedimentation, and the treatment with $TiCl_4$ is repeated one or more times. The solid is then washed with heptane or hexane and then dried.

The catalyst components obtained in this manner have the following properties:

- surface area = less than 100 m^2/g, preferably less than 80 m^2/g;
- porosity (nitrogen) = 0.20 - 0.50 ml/g;

- pore volume distribution such that more than 50% of the pores have a radius greater than 100 A.

The catalyst is obtained by mixing the solid catalyst component with an Al-trialkyl compound, preferably Al-triethyl or Al-triisobutyl.

The Al/Ti ratio is generally between 10 and 800.

The polymerization of ethylene and/or the other olefins is carried out according to known techniques operating in liquid phase or in the gas phase. The polymerization temperature is preferably between 70° and 90°C. The catalysts can be precontacted with small quantities of olefin (prepolymerization), maintaining the catalyst in suspension in a hydrocarbon solvent, polymerizing at a temperature between room temperature and 60°C, and producing quantities of polymer greater than 0.5 times the weight of the catalyst component.

The prepolymerization can also be carried out in liquid propylene, in which case quantities of polymer up to 1000 times the weight of the catalyst can be produced.

The resulting spherical polymer particles may be used in the preparation of masterbatches according to known techniques. One such technique involves permitting the polymer to absorb a solution or emulsion of the additive filler or pigment in a solvent, and then evaporating the solvent. The quantity of additive which remains incorporated depends on the concentration of the solution or emulsion itself. Another technique involves effecting the absorption of the additive or mixtures of additives in the melted form.

If the substances which constitute the additive, fillers, or pigments are solid and have a high melting point, said substances can be added in powder form to the polymer particles using paraffin oils or liquid wetting and surface-active agents such as liquid ethoxylated amines in order to obtain a good adhesion. It is preferable to use powders with a particle size lower than 10 μm.

In any case, masterbatches can be prepared very simply by feeding the polymer particles and at least one additive, pigment, filler or combinations thereof, in normal mixers for powders, and mixing for the desired residence time.

The preferred mixers are those having a velocity from about 150 rpm (for mixers with an internal volume of about 130 liters), up to 500 rpm (for mixers with a smaller internal volume of up to about 10 liters) which are thermoregulated. The use of thermoregulated mixers is particularly recommended.

The mixers are equipped with spray-feeders for the liquids, and hopper-feeders for the solids. The substances which can be fed in the molten state are normally melted in autoclaves under nitrogen.

When operating according to the above-mentioned methods one can obtain concentrations of additives, pigments, or fillers, or combinations thereof, up to 20%-30% by weight with respect to the total weight of the concentrate. Obviously these maximum values are not absolute, since when operating, for instance, with fillers having a high specific gravity, one can reach concentrations around 50% by weight. The minimum concentration value is a function of the additives, fillers, or pigments which are used, and of the concentration which one wants to obtain in the final products. In some cases it is possible to go down to a concentration of 5% by weight with respect to the total weight of the concentrate. Preferably, according to the invention, additives, fillers and/or pigments are contained in the spherical parts in an amount greater than 10% by weight.

The additives pigments and/or fillers that can be used are those normally added to polymers in order to impart desired properties. They include stabilizers, fillers, nucleating agents, slip agents, lubricant and antistatic agents, flame retardants, plasticizers, and blowing agents.

A large number of different grades of olefin polymers can be obtained in the form of spherical particles according to the invention. The polymers include high density polyethylenes (HDPE: density greater than 0.940), comprising copolymers of ethylene with alpha-olefins having from 3 to 12 carbon atoms; linear low-density polyethylenes (LLDPE: density less than 0.940); very low and ultra low density linear polyethylenes (VLLDPE and ULLDPE; density less than 0.920 and as low as 0.890), said LLDPE, VLLDPE and ULLDPE consisting of copolymers of ethylene and one or more alpha-olefins having from 3 to 12 carbon atoms, with a content of units derived from ethylene of over 80% by weight; crystalline polymers and copolymers of butene-1, 4-methyl-pentene-1, and styrene.

The data reported in the following examples are determined as indicated below:

Property	Method
- MIL flowability index	ASTM-D 1238
- Surface area	B.E.T. (apparatus used SORPTOMATIC 1800-C. Erba)
- Porosity (nitrogen)	B.E.T. (see above)
- Bulk density	DIN-53194
- Flowability	The time needed for 100 g of polymer to flow through a funnel with an outlet hole of 1.27 cm in diameter and the walls of which are inclined at 20°C to the vertical
- Morphology	ASTM-D 1921-63

The porosity expressed as percentage of voids is determined through absorption of mercury under pressure. The volume of mercury absorbed corresponds to the volume of the pores. In order to determine this, a dilatometer is used with calibrated probe (3 mm diam.) C D3 (C. Erba) connected to a mercury reservoir and a high vacuum rotating pump (1×10^2 mba).

A weighted quantity of the sample (about 0.5 g) is introduced into the dilatometer. The apparatus is then brought to a high vacuum (<0.1 mm Hg) and held for 10 minutes. The dilatometer is then connected to the mercury reservoir and the mercury is allowed to flow in slowly until it reaches the level marked on the probe at a height of 10 cm.

The valve that connects the dilatometer to the vacuum pump is closed and the apparatus is pressurized with nitrogen (2.5 kg/cm^2). The pressure causes the mercury to penetrate the pores and the level lowers in accordance with the porosity of the material. After the measure on the probe where the new mercury level has stabilized is determined, the volume of the pores is calculated as follows: $V = R^2\pi.\Delta H$ where R is the radius of the probe in cm, and ΔH is the difference in level in cm between the initial and final levels of the mercury column.

By weighing the dilatometer, dilatometer + mercury and dilatometer + mercury + sample, a value of apparent sample volume prior to pore penetration can be calculated. The volume of the sample is given by:

$$V1 = \frac{P1 - (P2 - P)}{D}$$

wherein

P is the weight of the sample in g;
P1 is the weight in g of the dilatometer + mercury;
P2 is the weight in g of the dilatometer + mercury + sample;
D is the density of the mercury (at 25°C = 13.546 g/cm^3)

The porosity percentage is given by:

$$x = \frac{100 \times V}{V1}$$

The following examples further illustrate the invention.

Example 1

A $MgCl_2 \cdot 3C_2H_5OH$ adduct in spherical particle form, which particles have a diameter from 30 to 150 microns, is prepared following the method described in Example 2 of U.S. Patent 4,399,054, operating at 5,000 rpm instead of 10,000 rpm. The resultant adduct is then dealcoholated by heating with temperature increasing from 50° to 100°C under a nitrogen stream until the alcohol content reaches 1.2 mole for each mole $MgCl_2$. The adduct thus obtained has a surface area of 11.5 m^2/g.

31.2 g of said adduct are added in a reaction vessel under agitation at 0°C to 625 ml of $TiCl_4$. Then the foregoing mixture is heated to 100°C for one hour. When the temperature reaches 40°C, diisobutyl phthalate is added in a molar ratio Mg/diisobutyl phthalate = 8. The contents of the vessel are then heated to 100°C for 1 hour, left to settle and subsequently the liquid is syphoned off hot. 500 ml of $TiCl_4$ are added, the solid and the contents of the vessel heated to 120°C for one hour, the reaction mixture is then left to settle and the liquid is syphoned off hot. The resulting solid is washed 6 times with 200 ml aliquots of anhydrous hexane at 60°C and then 3 times at room temperature. The solid catalyst component, after drying under vacuum, has the following characteristics:

- Ti content = 2.5% by weight;
- porosity (nitrogen) = 0.261 cm^3/g;
- surface area = 66.4 m^2/g.

Using 0.02 g of this solid, an ethylene polymerization is conducted in a 2.5 l stainless steel autoclave equipped with an agitator and a thermostatic system, which had been degassed with nitrogen at 70°C for one hour.

At 45°C there is introduced in H_2 stream 900 ml of a solution containing 0.5 g/l of Al-triisobutyl in anhydrous hexane and immediately afterwards, the catalyst component is suspended in 100 ml of the above-mentioned solution.

The temperature is rapidly brought to 75°C and H_2 is fed until the pressure reaches 3 atm, then ethylene is fed up to 10.5 atm. These conditions are maintained for 3 hours, replenishing continuously the ethylene depleted. At the end of the polymerization reaction, the autoclave is rapidly vented and cooled at room temperature.

The polymeric suspension is filtered and the solid residue dried in nitrogen at 60°C for 8 hours. 400 g of polyethylene are obtained with the following characteristics:

- MIE = 0.25 g/10';
- MIF = 7.8 g/10';
- MIF/MIE = 31.2;
- morphology = 100% spherical particles with diameter between 1000 and 5000 μm;
- flowability = 12 sec.;
- bulk density = 0.38 g/cm^3;
- void percentage = 30.

Example 2

By partially dealcoholating (as per Example 1) a $MgCl_2$3EtOH spherical adduct obtained according to the method indicated in the preceding example, an adduct is obtained with EtOH/$MgCl_2$ molar ratio of 0.15 with the following characteristics:

- porosity (mercury) = 1.613 cm^3/g;
- surface area = 22.2 m^2/g.

By treatment of the foregoing adduct with $TiCl_4$ at a temperature of 135°C (concentration = 50 g/l) for one hour three successive times, a spherical catalyst component is obtained which, after elimination of excess $TiCl_4$ by washing with n-hexane and subsequent drying, exhibits the following characteristics:

- Ti = 2% by wt.;
- porosity (nitrogen) = 0.435 cm^3/g;
- surface area = 44.0 m^2/g.

Using 0.012 of this component in the polymerization of ethylene as described in Example 1, 380 g of polyethylene are obtained with the following characteristics:

- MIE = 0.205 g/10';
- MIF = 16.42 g/10';
- MIF/MIE = 80.1;
- flowability = 12 sec.;
- bulk density = 0.40 g/cm^3;
- void percentage = 23.5%;
- morphology = 100% spherical particles with diameter between 1000-5000 μm.

Example 3

20 kg of polyethylene in spherical particle form obtained with a continuous ethylene polymerization test using a catalyst obtained from solid catalyst component and co-catalyst components of Example 1 are introduced into a Loediga FM 130 P mixer lined with steam at 100°C and mixed for 5 minutes at a blade speed of 150 rpm until the temperature of the polymer reaches 70°C. 5 kg of Atmer 163 product (Atlas) are then sprayed into the mixer at 100°C. The agitation is continued for 15 minutes and then the product is discharged. The polymer thus obtained is in the form of spherical particles with 100% of the particles having a diameter from 1000 to 5000 microns which particles contain 19.8% by weight of Atmer product and have a flowability of 13 sec.

Claims

Claims for the following Contracting States : AT, BE, DE, DK, FR, GB, IT, NL, PT, SE

1. Crystalline copolymers of (1) an olefin of the formula CH_2=CHR, wherein R is hydrogen, an alkyl radical having 2 to 6 carbon atoms, or aryl and with (2) another different olefin of said formula or with propylene, provided that when propylene is one of the olefins, it is present in an amount of less than 30% by weight and when ethylene is one of

the olefins, it is present in an amount greater than 80% by weight, said copolymers being in the form of spherical particles with an average diameter between 50 and 5000 µm and a porosity expressed in void percentage greater than 15%.

2. The spherical particles of claim 1, wherein more than 40% of the pores have a diameter greater than one µm.

3. The spherical particles of claim 1, wherein more than 90% of the pores have a diameter greater than one µm.

4. The spherical particles of claim 1, wherein the void percentage is between 20 and 40%.

5. The spherical particles of claim 1 containing additives, fillers and/or pigments in an amount greater than 10% by weight.

Claims for the following Contracting State : ES

1. Use of crystalline copolymers of (1) an olefin of the formula CH_2=CHR, wherein R is hydrogen, an alkyl radical having 2 to 6 carbon atoms, or aryl and with (2) another different olefin of said formula or with propylene, provided that when propylene is one of the olefins, it is present in an amount of less than 30% by weight and when ethylene is one of the olefins, it is present in an amount greater than 80% by weight, for the manufacture of spherical particles with an average diameter between 50 and 5000 µm and a porosity expressed in void percentage greater than 15% for the preparation of masterbatches containing significant quantities of pigment and/or additives.

2. Use according to claim 1, wherein more than 40% of the pores have a diameter greater than one µm.

3. Use according to claim 1, wherein more than 90% of the pores have a diameter greater than 1 µm.

4. Use according to claim 1, wherein the void percentage is between 20 and 40%.

5. Use according to claim 1, wherein the spherical particles contain additives, fillers and/or pigments in an amount greater than 10% by weight.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, DE, DK, FR, GB, IT, NL, PT, SE

1. Kristalline Copolymere aus (I) einem Olefin der Formel CH_2=CHR, in welcher R Wasserstoff, ein Alkylradikal mit 2 bis 6 Kohlenstoffatomen oder ein Arylrest ist und mit (2) einem weiteren unterschiedlichen Olefin dieser Formel oder mit Propylen, unter der Voraussetzung, daß, wenn Propylen eines der Olefine ist, es in einem Gehalt von weniger als 30 Gew.-% vorliegt und wenn Ethylen eines der Olefine ist, es in einem Gehalt von über 80 Gew.-% vorliegt, wobei das Copolymer die Form von kugelförmigen Teilchen mit einem mittleren Durchmesser zwischen 50 und 5000 µm und einer Porosität, ausgedrückt als Prozentsatz an leerem Raum, von größer als 15% aufweist.

2. Kugelförmige Teilchen nach Anspruch 1, in welchen über 40% der Poren einen Durchmesser von mehr als 1 µm aufweisen.

3. Kugelförmige Teilchen nach Anspruch 1, in welchen über 90% der Poren einen Durchmesser von größer als 1 µm aufweisen.

4. Kugelförmige Teilchen nach Anspruch 1, in welchen der Prozentsatz an leerem Raum zwischen 20 und 40% liegt.

5. Kugelförmige Teilchen nach Anspruch 1, welche Zusatzstoffe, Füllstoffe und/oder Pigmente in einem Gehalt von größer als 10 Gew.-% enthalten.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verwendung eines kristallinen Copolymers aus (1) einem Olefin der Formel CH_2=CHR, in welcher R Wasserstoff, ein Alkylradikal mit 2 bis 6 Kohlenstoffatomen oder ein Arylrest ist und mit (2) einem weiteren unterschiedlichen Olefin dieser Formel oder mit Propylen, unter der Voraussetzung, daß, wenn Propylen eines der Olefine ist, es in einem Gehalt von weniger als 30 Gew.-% vorliegt und wenn Ethylen eines der Olefine ist, es mit einem Gehalt von größer als 80 Gew.- vorliegt, für die Herstellung von kugelförmigen Teilchen mit einem mittleren Durchmesser zwischen 50 und 5000 µm und einer Porosität, ausgedrückt als Prozentsatz an leerem Raum, von größer als 15% für die Herstellung von Masterbatches mit erheblichen Mengen von Pigmenten und/oder Zusatzstoffen.

2. Verwendung nach Anspruch 1, wobei über 40% der Poren einen Durchmesser von mehr als 1 µm aufweisen.

3. Verwendung nach Anspruch 1, wobei mehr als 90% der Poren einen Durchmesser von über 1 µm aufweisen.

4. Verwendung nach Anspruch 1, wobei der Prozentsatz an leerem Raum zwischen 20 und 40% liegt.

5. Verwendung nach Anspruch 1, wobei die kugelförmigen Teilchen Zusatzstoffe, Füllstoffe und/oder Pigmente in einem Gehalt von über 10 Gew.-% enthalten.

Revendications

Revendications pour les Etats contractants suivants : AT, BE, DE, DK, FR, GB, IT, NL, PT, SE

1. Copolymères cristallins de (1) une oléfine répondant à la formule CH_2=CHR, dans laquelle R représente un atome d'hydrogène, un radical alkyle contenant de 2 à 6 atomes de carbone ou encore un radical aryle et avec (2) une autre oléfine différente de celle répondant à ladite formule ou avec du propylène à condition que, lorsque le propylène représente une des oléfines, il soit présent en une quantité inférieure à 30% en poids et, lorsque l'éthylène représente une des oléfines, il soit présent en une quantité supérieure à 80% en poids, lesdits copolymères étant présents sous la forme de particules sphériques possédant un diamètre moyen entre 50 et 5000 µm et une porosité exprimée en pourcentage de vide supérieure à 15%.

2. Particules sphériques selon la revendication 1, dans lesquelles plus de 40% des pores possèdent un diamètre supérieur à 1 µm.

3. Particules sphériques selon la revendication 1, dans lesquelles plus de 90% des pores possèdent un diamètre supérieur à 1 µm.

4. Particules sphériques selon la revendication 1, dans lesquelles le pourcentage de vide se situe entre 20 et 40%.

5. Particules sphériques selon la revendication 1, contenant des additifs, des matières de remplissage et/ou des pigments en une quantité supérieure à 10% en poids.

Revendications pour l'Etat contractant suivant : ES

1. Utilisation de copolymères cristallins de (1) une oléfine répondant à la formule CH_2=CHR, dans laquelle R représente un atome d'hydrogène, un radical alkyle contenant de 2 à 6 atomes de carbone ou encore un radical aryle et avec (2) une autre oléfine différente de celle répondant à ladite formule ou avec du propylène à condition que, lorsque le propylène représente une des oléfines, il soit présent en une quantité inférieure à 30% en poids et, lorsque l'éthylène représente une des oléfines, il soit présent en une quantité supérieure à 80% en poids, pour la fabrication de particules sphériques possédant un diamètre moyen entre 50 et 5000 µm et une porosité exprimée en pourcentage de vide supérieure à 15% pour la préparation de mélanges-mères contenant des quantités importantes de pigments et/ou d'additifs.

2. Utilisation selon la revendication 1, dans laquelle plus de 40% des pores possèdent un diamètre supérieur à 1 µm.

3. Utilisation selon la revendication 1, dans laquelle plus de 90% des pores possèdent un diamètre supérieur à 1 µm.

4. Utilisation selon la revendication 1, dans laquelle le pourcentage de vide se situe entre 20 et 40%.

5. Utilisation selon la revendication 1, dans laquelle les particules sphériques contiennent des additifs, des matières de remplissage et/ou des pigments en une quantité supérieure à 10% en poids.